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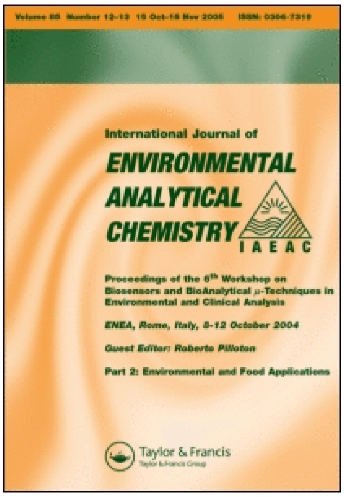

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Determination of Low Levels of Nitrates in Natural Waters by Direct Potentiometry Using an Ion Selective Electrode of Improved Sensitivity

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DETERMINATION OF LOW LEVELS OF NITRATES IN NATURAL WATERS BY DIRECT POTENTIOMETRY USING AN ION SELECTIVE ELECTRODE OF IMPROVED SENSITIVITY

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This work describes the construction and the evaluation of a nitrate potentiometric transducer with improved sensitivity and it application to the determination of low levels of nitrate in natural waters. The results obtained in these determinations were evaluated comparatively with those obtained by the conventional ion-selective electrodes and by the reference methods which include colourimetric measurement.

The construction of the developed units closely follows that used for the conventional ones, but using a circuit that performs the summing of the potentials supplied by the two sensor membranes.

The quality of these units response was assessed evaluating their lower limit of response and detection, sensitivity, potential stability, selectivity coefficients, response time and pH effect. The results obtained by potentiometric methodologies, using ISEIS, offer precision values higher to those given by units of common sensitivity.

A comparative study of the results obtained by potentiometry, using both types of units, and the conventional method was made in the determination of nitrate in natural waters. It showed that, in samples with concentrations of nitrate anions comprised between 0.24 and 2.8 μg/l, the results given by the improved sensitivity units (relative deviation less than 2.6 %) were more precise than those given by the common sensitivity electrodes (relative deviation less than 11 %).

Keywords: Ion selective electrodes; improved sensitivity; nitrate; natural waters

INTRODUCTION

The use of ion selective electrodes (ISE) is nowadays accepted for the determination of many species in the most diverse matrices, namely water[1].

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A significant limitation to the use of the ISE in water analysis derives from the values of their practical limits of detection[2] that do not allow to perform measurements in such reduced concentrations, as it would be desirable, to control the primary species, becoming necessary to extend the determinations to a non-linear range, but reproducible in the response curve.

Not less significant are the limitations connected with the use of ISE's as the minor error in the determination of potentials at the corresponding concentration values. For example an error of about ± 0.5 mV in measuring a potential corresponds to a relative error in concentration, of approximately 2% in the case of electrodes sensitive to charge 1 species, and of approximately 4% for those sensitive to charge 2 ions.[3–5]

It is possible to find references in literature that refer trends to overcome this kind of problem, namely the use of cells connected in series[6–8] or by totalling the potentials of two conventional electrodes immersed in the same vessel[9–11].

This work refers to the construction of a potentiometric transducer sensitive to nitrate, which comprises two sensor membranes placed in the same electrode body, where the potential is given out by each of them in relation to the same reference electrode and then added externally by a summing operational amplifier.

The construction process used is based on a procedure developed and presented by some of us in previous papers[12], which consists of ion-selective electrodes of mobile conductor without an inner reference solution[13]. In this construction process the membrane is directly applied over the conductive support based on a graphite/epoxy resin mixture.

The transducer was constructed with plastic membranes sensitive to nitrate anions and its analytical efficiency was tested by performing determinations of nitrate in different types of water with different nitrate concentrations, which were close to the lower limit of linear response.

Determinations of the same species were performed simultaneously, for comparative results, using a conventional shaped ion-selective electrode and a spectrophotometric process.[14]

EXPERIMENTAL

All chemicals used were of analytical reagent grade and were not submitted to any additional purification except in the case of the KNO_3 in the preparation of the standards, which were dried at 110°C overnight.

The ionic strength adjuster solution comprised $Pb(CH_3COO)_2$ 0.02 *M*, PbO 0.01 *M*, CH_3COOK 0.02 *M*, NH_2SO_3H 0.01 *M*, with a final pH of 6.8 units.[15]

The water used in the preparation of all solutions was bi-deionised, with a conductivity lower than 0.1 $\mu S.cm^{-1}$.

Reference Procedure

The reference methodology used in the determination of nitrate was suggested by ASTM [14] for natural waters, using the reaction between nitrate and sodium salicylate. The yellow coloration obtained was measured using a spectrophotometer at 420 nm.

Apparatus and Electrodes

The potential measurements were determined by using a high impedance Crison Model 2002 pHmeter. The addition of solutions was accomplished by using Crison Model 2031 automatic burettes.

The equipment control and the data acquisition was done using a Unisys PW300 computer, connected to an Epson Model LX800 dot matrix printer and an Advantech PCLabcard 714 analogue-to-digital converter card.

As in most of the tests, the determinations were performed simultaneously by different electrodes, to facilitate their selection. A home-made electrode switch was used, controlled by a microcomputer.[16] As reference electrode an Orion Model 900200 double-junction electrode was used, with a KCl saturated solution in the inner compartment and a Na_2SO_4 0.033 *M* solution in the external.

In the evaluation of proton interference, the pH measurements were performed using an Ingold ref. 10/402 glass electrode. The potentiometric measurements were performed in a double wall vassel, through where water at 25.0 ± 0.2°C was circulated. The spectrophotometric measurements for the reference procedure were performed using a Hitachi Model U-2000 Spectrophotometer.

Construction of ISE of Improved Sensitivity

The construction of ISE of improved sensitivity (ISEIS) was similar to the one used for the construction of electrodes of conventional shapes, but without an inner reference solution, and with a plastic membrane applied directly over a conductor support, made of a graphite mixture with an epoxy resin.[15, 16]

The shape and dimension of the ISEIS units were similar to those of conventional configuration, however in their extremes two semicircular membranes were placed, responsible for the potentials that were measured against an unique reference (Figure 1).

The sensor system used in the preparation of the membrane was composed of a tris(4,7-diphenyl-1,10-phenantroline) nickel (II) complex dissolved in a p-nitrocumene solution (7% of sensor and 62% of solvent mediator). The ionic exchanger was synthesised using the procedure referred by Hulanicki.[17]

The application of the two membranes on the extremes of the ISEIS, divided in approximately two equal parts, was made by replicate applications of the solution membrane in tetrahydrofuran over the conductive supports of the two halves. Each application was performed with intervals of one hour, which was the necessary time for the, at least partial, evaporation of the tetrahydrofuran of the previous application. Once the semicircular membrane cavities were filled, they were left exposed to air for about 24 hours to guarantee a complete tetrahydrofuran evaporation. Finally, the membranes were placed during 48 hours in KNO_3 0.1*M*, for conditioning.

The potentials given out by each of the membranes were measured against the same reference electrode, and the values were added by an external circuit before being applied to the pHmeter.

The summing device (Figure 2) was composed of two following stages and one summing stage, having used in the first stages very high input impedance operational amplifiers.[18] The whole set-up was installed in a metallic box together with a symmetric power supply source of ± 9 V.

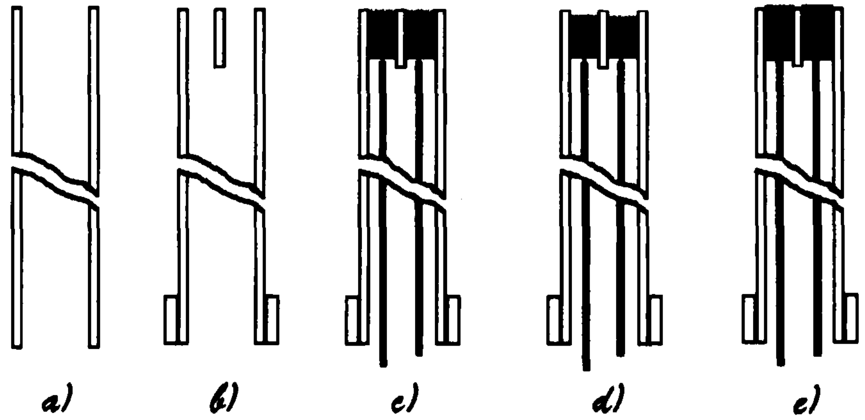

FIGURE 1 ISEIS construction phases. a) body; b) septum; c) conductor support and shielded cables; d) membranes cavities; e) membranes.

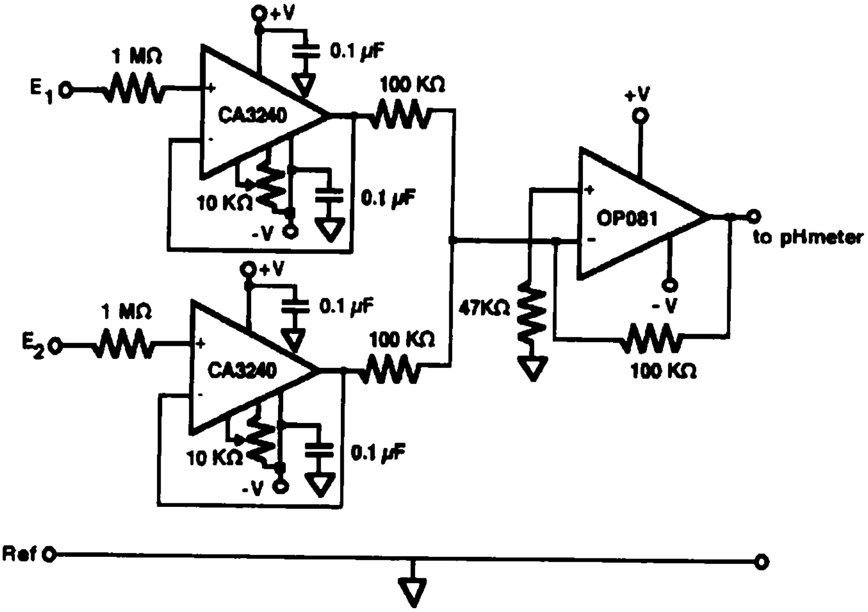

FIGURE 2 Schematic diagram of the summing circuit.

RESULTS AND DISCUSSION

Working Characteristics of the ISEIS

The evaluation of the working characteristics, of the ion-selective electrodes with improved sensitivity, was assessed by well-established procedures, using conventional shape ion-selective electrodes[2]

From the repeated plotting of the calibration curves, for a range of concentrations between 10^{-6} and 10^{-1} *M*, covering the linear and the non-linear response zones, it was possible to determine, according to IUPAC recommendations, the lower limit of linear response, the practical limit of detection, the slope, the potential stability, and the electrodes lifetime (Table I). This assessment showed that the working characteristics of ISEIS were generically similar to those of the selective electrodes, using the same type of membrane (Table I), except in what refers to sensitivity, which naturally presented an increase (slope was nearly the double in the zone of linear response).

The evaluation of the potentials stability in that period showed that it did exist a reasonable stability of behaviour during the whole work. Despite of the lower standard deviation shown by the conventional shaped units, the ISEIS showed a relative standard deviation lower than the former.

TABLE I Working characteristics of the ISEIS and ISE

	ISEIS		*ISE*	
Detection limit	1×10^{-5}		1×10^{-5}	
Lower limit of linear response	5×10^{-5}		6×10^{-5}	
Effective pH range[1]	2 − 9		2 − 9	
Slope[2]	-114 ± 1		-56.0 ± 0.9	
Response time[3]	< 1 min		< 1 min	
Operational lifetime	> 6 months		> 6 months	
Potential stability[4]	< 1.4 mV		< 1.0 mV	
Selectivity coefficients[5]				
	[X], *M* 1×10^{-3}			
Ion (X)	1×10^{-3}	1×10^{-2}	1×10^{-3}	1×10^{-2}
Cl^-	9.5×10^{-3}	3.6×10^{-4}	9.5×10^{-3}	3.8×10^{-4}
SO_3^{2-}	1.1×10^{-3}	6.7×10^{-4}	1.3×10^{-3}	7.2×10^{-4}
NO_2^-	1.4×10^{-1}	7.1×10^{-2}	1.4×10^{-1}	9.1×10^{-2}

1—$[NO_3^-] = 10^{-3}$; 2—mV/log$[NO_3^-]$; 3—10^{-3} to 10^{-2} *M*; 4—During a working day; 5—Separate solutions method

The results obtained with ISEIS units, during a working day, indicated standard deviations inferior to 2 mV, for concentration values of 10^{-5} *M* and inferior to 1mV for concentration values of 10^{-4} *M* with an average of 1.4 mV.

The evaluation of the selectivity showed an accentuated interference in the case of chloride and, due to the almost constant presence of this anion in natural waters, the use of conditioning solutions which was the usual procedure in this type of determination, was compulsory.

Determination of Nitrate in Natural Waters

The determinations were performed with samples of natural water, using 20 mL of water, to what 20 mL of ionic strength adjuster were added (see experimental part).

The results obtained with conventional and with ISEIS units were compared with the results obtained by the reference method. As it can be observed (Table II), the correlation between the results is reasonable, being however superior in the case of the ISEIS units in relation to the conventional units.

It should be noticed that, at the zone of non linear response, the deviations to the values obtained with the reference method are higher related to those obtained with conventional units.

TABLE II Results obtained by direct potentiometry with ISEIS and ISE and conventional procedure (average of five determinations and standard deviation) for nitrate in natural waters

	Reference			*ISEIS*				*ISE*			
Sample	*mg/L*	$[NO_3^-]\cdot M.10^{-5}$	*RSD*[1]. 10^{-6}	*mg/L*	$[NO_3^-]\cdot M.10^{-5}$	*RSD*[1]. 10^{-6}	*RD%*[2]	*mg/L*	$[NO_3^-]\cdot M.10^{-5}$	*RSD*[1]. 10^{-6}	*RD%*[2]
1	2.82	4.54	2.43	2.79	4.50	3.41	−0.85	2.73	4.40	1.55	−3.1
2	2.63	4.24	3.32	2.58	4.16	1.55	−1.8	2.77	4.46	2.37	5.2
3	0.746	1.20	19.4	0.727	1.17	0.377	−2.6	0.761	1.23	0.449	2.0
4	0.524	0.845	2.25	0.528	0.852	1.41	0.84	0.481	0.776	0.590	−8.1
5	0.492	0.794	3.28	0.491	0.792	0.277	−0.20	0.448	0.723	0.209	−8.9
6	0.558	0.900	0.971	0.544	0.877	0.347	−2.5	0.519	0.837	0.305	−6.9
7	0.284	0.458	0.238	0.287	0.463	0.303	1.0	0.262	0.423	0.187	−7.7
8	0.524	0.845	0.731	0.533	0.860	0.281	1.8	0.564	0.910	0.591	7.7
9	1.55	0.250	7.33	1.53	2.47	0.995	−1.1	1.64	2.65	1.25	5.9
10	0.661	0.107	1.74	0.664	1.07	0.538	0.53	0.621	1.00	0.266	−6.1
11	0.233	0.375	0.459	0.237	0.382	0.215	1.9	0.245	0.395	0.319	5.3
12	0.626	1.01	0.871	0.617	0.995	0.317	−1.5	0.576	0.929	0.586	−8.0

[1] Relative standard deviation (*M*)

[2] Relative deviation to reference procedure

CONCLUSIONS

From the obtained results, it can be concluded that the use of the nitrate selective electrode with improved sensitivity, when used in the dosage of that ion in natural waters, is preferable to the use of the common sensitivity units, once it gives more similar results than those obtained with the reference methodology, which, by the slowness and the handling of the used chemicals, is to be superseded in favour of the potentiometric methodologies.

Therefore, since the potentiometric methodologies are very rapid and easy to perform, they present a favourable alternative either in terms of manual methodologies or in terms of automatization.

The construction process used for obtaining ISEIS units does not differ significantly from the one used for the common sensitivity units. There is the fact of the compulsory use of a summing circuit, but it can easily be constructed by qualified personnel. Finally, it must be stressed that the increase of precision, that is possible to obtain with this kind of device, justifies its preference in detriment of the common sensitivity units.

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